

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 893 248 A1

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:

27.01.1999 Bulletin 1999/04

(51) Int. Cl.⁶: **B32B 27/36**, **B60J 1/00**,

B60J 3/06

(21) Application number: **97913492.1**

(86) International application number:

PCT/JP97/04397

(22) Date of filing: **02.12.1997**

(87) International publication number:

WO 98/26929 (25.06.1998 Gazette 1998/25)

(84) Designated Contracting States:

DE FR GB IT LU NL

(72) Inventor:

ENDO, Kazuo

Diafoil Hoechst Co. Ltd.,

Shiga-ken (JP)

(30) Priority: **17.12.1996 JP 337007/96**

(71) Applicant:

Mitsubishi Polyester Film Corporation

Tokyo 108 (JP)

(74) Representative:

ter Meer, Nicolaus, Dipl.-Chem., Dr.

TER MEER STEINMEISTER & PARTNER GbR,

Patentanwälte,

Mauerkircherstrasse 45

81679 München (DE)

(54) ORIENTED LAMINATED POLYESTER FILM TO BE PASTED ON AUTOMOBILE WINDOWPANES

(57) The present invention relates to an oriented laminated polyester film for pasting on car windows, comprising at least three layers including intermediate layer(s) being incorporated with a dye, which laminated polyester film satisfies the following conditions simultaneously:

the ratio of the dye concentration (%) in the outermost layers on both sides (CA) to the dye concentration (%) in the intermediate layer (CB) being not more than 0.5,

the ratio of the sum of the thicknesses (μm) of the outermost layers (DA) to the overall thickness (μm) of the whole layers (DZ) being 0.02 to 0.8,

the heat shrinkage (%) in the machine direction and transverse direction of the film when heat-treated at 180°C for 5 minutes (SMD and STD) being 1.0 to 5.0% and not more than 2.0%, respectively,

the center line average roughness (μm) of the film surface (Ra) being 0.005 to 0.05 μm , and the film haze (H, %) being not more than 5%.

This laminated film is free from the problem of contamination by the dye during manufacture thereof, shows excellent workability when applied curved glass of an automobile, and also has excellent transparency.

EP 0 893 248 A1

Description

TECHNICAL FIELD

5 The present invention relates to an oriented laminated polyester film for pasting on car windows. More particularly, it relates to an oriented laminated polyester film for pasting on car windows, which polyester film has a dye-incorporated intermediate layer(s).

BACKGROUND OF ART

10 Recently, attention is focused on the laminated polyester films having a dye-incorporated intermediate layer(s), for pasting on car windows. In such laminated films, there is a problem that the casting rolls, longitudinal stretching rolls and tenters during manufacture of the films are contaminated due to the sublimation property of the dye even if a dye with high heat resistance is selected.

15 In Japanese Patent Application Laid-Open (KOKAI) No. 8-230126, in order to solve the above problem, the present inventor has proposed an oriented laminated polyester film for pasting on car window, which polyester film comprises at least three layers comprising two outermost layers containing no dye and an intermediate layer containing a dye, the film satisfying the following three formulae ① to ③ simultaneously.

$$20 \quad 0.02 \leq IB-IA \leq 0.10 \quad \text{①}$$

$$0.05 \leq dA/dB \leq 0.45 \quad \text{②}$$

$$25 \quad 0.05 \leq TA/TB \leq 0.60 \quad \text{③}$$

30 In the above formulae, IA represents a viscosity of the polyester composition forming the intermediate layer, IB represents a viscosity of the polyester composition forming both outermost layers, dA represents thickness (μm) of the intermediate layer, dB represents thickness (μm) of the outermost layers, TA represents a visible light transmittance (%) of the intermediate layer, and TB represents a visible light transmittance (%) of the outermost layers.)

35 As seen from a film thickness of $10.5 \mu\text{m}/4 \mu\text{m}/10.5 \mu\text{m}$ shown in the Examples of the above Japanese patent application, the thickness of the intermediate layer of the said laminated film is smaller than the thickness of the outermost layers in due to the definition of the above formula ②. This thickness relation is based on the reason that sublimation of the dye can be prevented by sandwiching the dye-containing intermediate layer between the relatively thick outermost layers.

40 However, the laminated film based on the above conception, that is, the intermediate layer being smaller in thickness than the outermost layers, involves the following problem. Namely, the dye concentration necessary for obtaining a film of high light screening effect is increased, and consequently, the film haze is elevated because of clouding caused by precipitation of the undissolved dye.

As for the method of pasting (sticking) the said laminated film on curved car window glass, the conventional method comprising pasting several strips of laminated film is being superseded by the one-piece pasting method which is advantageous in cost and appearance. In this case, it is required to prevent wrinkling of the film when it is pasted on a car window. Also, the laminated film is required to have excellent transparency.

45 However, the laminated film proposed in the said Japanese patent application is not improved in wrinkle resistance and transparency.

DISCLOSURE OF THE INVENTION

50 The present invention has been made in view of the above circumstances, and the object of the present invention is to provide an oriented laminated polyester film for pasting on car window, which film is free from the problem of sublimation of the dye in the film manufacturing process and is also excellent in workability on application to curved car window glass and excellent in transparency.

55 As a result of the present inventor's earnest studies, the present it has been found that by forming a film having a specific layer structure, it is possible to prevent sublimation of the dye in the film manufacturing process and imparts the specific properties to the film, so that workability and transparency can be improved. The present invention has been attained on the basis of the above finding.

In an aspect of the present invention, there is provided an oriented laminated polyester film for pasting on car win-

dow, comprising at least three layers including intermediate layer(s) being incorporated with a dye, which laminated polyester film satisfies the following formulae ① to ⑥ simultaneously:

$$CA/CB \leq 0.5 \quad \text{①}$$

$$0.02 \leq DA/DZ \leq 0.8 \quad \text{②}$$

$$1.0 \leq SMD \leq 5.0 \quad \text{③}$$

$$STD \leq 2.0 \quad \text{④}$$

$$0.005 \leq Ra \leq 0.05 \quad \text{⑤}$$

$$H \leq 5 \quad \text{⑥}$$

wherein CA represents a dye concentration (%) in the outermost layers on both sides, in case where the dye concentrations in the outermost layers are different, CA represents a dye concentration the outermost layer with a higher dye concentration; CB represents a dye concentration (%) in the intermediate layer, in case where there exist plural intermediate layers, CB represents an average of the dye concentrations in the layers excluding the outermost layers on both sides; DA represents a sum of the thicknesses (μm) of the outermost layers; DZ represents an overall thickness (μm) of the whole layers; SMD represents a heat shrinkage (%) in the machine direction of the film when heat-treated at 180°C for 5 minutes; STD represents a heat shrinkage (%) in the transverse direction of the film when heat-treated at 180°C for 5 minutes; Ra represents a center line average roughness (μm) of the film surface; and H represents a film haze (%).

The present invention is described in detail, hereinafter.

The laminated polyester film according to the present invention is produced by stretching the sheet obtained by co-extrusion method and heat-setting it as required. Hereinafter, the present invention is described by showing an embodiment where the film is constituted in a three-layer structure.

The polyester used in the present invention is the one obtained by reacting an aromatic dicarboxylic acid or an ester thereof with a glycol as principal starting materials. Especially, polyesters in which not less than 80% of the repeating structural units are constituted by the ethylene terephthalate units or ethylene-2,6-naphthalate units, are preferred. Such polyesters may contain a third component.

As the aromatic dicarboxylic acid, there can be used, beside terephthalic acid and 2,6-naphthalene dicarboxylic acid, for instance, isophthalic acid, phthalic acid, adipic acid, sebacic acid and oxycarboxylic acids (such as p-oxyethoxybenzoic acid). As the glycol, there can be used, beside ethylene glycol, for instance, one or more of diethylene glycol, propylene glycol, butanediol, 1,4-cyclohexanedimethanol, neopentyl glycol and the like.

In the present invention, the "outermost layers" are the layers which constitute the two exposed sides of the film. The other layers are all called "intermediate layers". The intrinsic viscosity (IV) of the polyester of the respective layers is usually 0.52 to 0.75, preferably 0.55 to 0.70, more preferably 0.58 to 0.67. If the IV is less than 0.52, it may be difficult to obtain a film having excellent heat resistance and mechanical strength, while if the IV exceeds 0.75, the extrusion step in the film producing process may be overloaded, causing a drop of productivity.

The overall thickness of the laminated film of the present invention is usually 10 to 50 μm , preferably around 25 μm .

In the laminated film of the present invention, the ratio of dye concentration (CA) of the outermost layers to dye concentration (CB) of the intermediate layer(s) (CA/CB) is not more than 0.5, preferably not more than 0.3, more preferably not more than 0.1, even more preferably not more than 0.05. When the CA/CB ratio exceeds 0.5, the dye may tend to sublime in the film manufacturing process, causing contamination of the film production line.

Also, in the laminated film of the present invention, the ratio of the sum of the thicknesses (DA) of the outermost layers to the overall thickness (DZ) of the film (DA/DZ) is 0.02 to 0.8, preferably 0.08 to 0.6, more preferably 0.15 to 0.5. When the DA/DZ ratio is less than 0.02, it may be difficult to satisfactorily prevent sublimation of the dye in the intermediate layer during heat-setting in the film producing process. In case where the DA/DZ ratio exceeds 0.8, the intermediate layer becomes too thin, the dye content required for obtaining a film of high light-screening performance increases too excess. Consequently, the film haze may be elevated due to clouding caused by precipitation of the undissolved dye, and further, the intrinsic viscosity of the polyester may lower, resulting in the loss of characteristic properties of the

polyester itself, or the thickness of the intermediate layer may become non-uniform to cause color shading.

As the dye to be contained in the intermediate layer, anthraquinone dyes, phthalocyanine dyes and the like are preferred in terms of chemical structure in view of heat resistance and dispersibility. Disperse dyes and oil-soluble dyes are preferred from the viewpoint of dyeing workability. Usually, several different types of these dyes are properly selected and mixed for use, with the dye content in the polyester, of preferably 0.01 to 10% by weight.

In the outermost layers of the laminated film of the present invention, preferably the fine inactive particles are added to roughen the film surface to impart an appropriate degree of slipperiness to the film, thereby to improve film workability in the film take-up step, the coating step for forming a hard coat described later, and the step for pasting the film with car window glass.

The average size of the fine inactive particles used for the said purpose in the present invention is usually 0.5 to 3.0 μm , preferably 0.8 to 2.0 μm . When the average particle size is less than 0.5 μm , the film workability tends to lower, and when the average particle size exceeds 3.0 μm , the planarity and transparency of the film surface may be impaired. The amount of such fine inactive particles added is usually 0.005 to 1.0 wt%, preferably 0.01 to 0.7 wt% based on the weight of outermost layer. When the amount of the particles added is less than 0.005 wt%, the winding properties of the film tend to deteriorate, and when the particle amount exceeds 1.0 wt%, the film surface tends to be roughened to excess, adversely affecting film transparency.

Examples of the fine inactive particles usable in the present invention include fine particles of silicon oxide, titanium oxide, zeolite, silicon nitride, boron nitride, cerite, calcium carbonate, magnesium carbonate, barium carbonate, calcium sulfate, barium sulfate, calcium phosphate, lithium phosphate, magnesium phosphate, lithium fluoride, aluminum oxide, silicon oxide, titanium oxide, kaolin, talc, carbon black, and fine crosslinked polymer particles such as disclosed in Japanese Patent Publication (KOKOKU) No. 59-5216. Two or more different types of these fine inactive particles may be used in admixture.

The method for containing such inactive particles and dye in the polyester is not specified in the present invention; it is possible to adopt, for example, a method of adding the inactive particles and dye in the polymerization step or a method of incorporating the particles and dye in the polyester to form a masterbatch by using an extruder.

In practical use of the laminated film of the present invention, it is provided with a hard coat layer on the outermost layer which forms surface side when the film is pasted on a car window. Hard coating is utilized in many fields of industrial products for improving scuff resistance of the products, and various types of photopolymers represented by acrylic resins are known as hard coating polymers.

When a hard coat such as mentioned above is directly formed on the surface of a polyester film, satisfactory adhesion may not be provided. So, in the laminated film of the present invention, it is preferred to provide an enhanced adhesion layer to the hard coat. As the coating layer forming agent, there are preferably used water-soluble or water-dispersible polyester-based compositions, polyurethane-based compositions, polyacryl-based compositions, styrene-butadiene copolymer, acrylonitrile-butadiene copolymer and the like.

A crosslinking agent may be contained in the said coating layer to improve blocking resistance, water resistance, solvent resistance and mechanical strength. The crosslinking agents usable in the present invention include hydroxymethylated or hydroxyalkylated urea-based, melamine-based, guanamine-based, alkylamide-based and polyamide-based compounds, epoxy compounds, oxazoline compounds, aziridine compounds, blocked isocyanate compounds, silane coupling agents, dialcohol aluminate-based coupling agents, zirco-aluminate-based coupling agents, peroxides, heat- or light-reactive vinyl compounds, and photosensitive resins.

The said coating layer may contain fine particles for improving slip properties. Such fine particles may be either inactive inorganic particles or organic particles. Examples of the inactive inorganic particles include colloidal silica, alumina, calcium carbonate and titanium dioxide, and the examples of the organic particles include the fine particles obtained from polystyrene-based resins, polyacryl-based resins and polyvinyl-based resins, and their crosslinked particles.

The coating solution used for forming the coating layer may contain defoaming agent, coating properties improver, thickener, low-molecular antistatic agent, organic lubricant, antioxidant, ultraviolet absorber, foaming agent, dye, pigment, etc., if necessary. Further, in case where water is used as the main medium, the coating solution may contain a small quantity of an organic solvent for the purpose of improving water dispersibility or film-forming properties. Preferably an organic solvent is used in such an amount range where the solvent can be dissolved in water.

Examples of the organic solvents usable in the present invention include aliphatic or alicyclic alcohols such as n-butyl alcohol, n-propyl alcohol, isopropyl alcohol, ethyl alcohol and methyl alcohol; glycols such as ethylene glycol, propylene glycol and diethylene glycol; glycol derivatives such as n-butyl cellosolve, ethyl cellosolve, methyl cellosolve and propylene glycol monomethyl ether; ethers such as dioxane and tetrahydrofuran; esters such as ethyl acetate and amyl acetate; ketones such as methyl ethyl ketone and acetone; and amides such as N-methylpyrrolidone. These organic solvents may be used as a mixture of two or more of them.

The coating layer thickness, after drying, is usually 0.02 to 0.5 μm , preferably 0.01 to 0.3 μm , more preferably 0.03 to 0.2 μm . When the coating layer thickness exceeds 0.5 μm , the film may tend to blocking, and especially when the

coated and stretched film is re-stretched for elevating the film strength, the film tends to adhere to the rolls in the stretching operation. When the coating layer thickness is less than 0.02 μm , its adhesion improving effect tends to diminish.

In order to improve coating properties and adhesion of the coating layer to the film, the film may be subjected to a chemical treatment or a discharge treatment before coating. Also, the discharge treatment may be applied on the coating layer side of the film after coating for improving the surface properties of the coating layer.

As for the method for forming such a coating layer, there are usable a system A in which the coating layer is formed in the process of producing a biaxially stretched film, and a system B in which the coating layer is formed after biaxial stretching, and the system A is preferred. The system A also includes a method in which a thin film forming solution is first applied on the surface of a non-stretched film and the coated film is stretched biaxially, and the method in which a thin film forming solution is applied on the surface of a monoaxially stretched film and then the film is further stretched in the direction orthogonal to the initial stretching direction. It is also preferred to use a combination of these methods.

For coating, there can be used various types of coater, such as reverse roll coater, gravure coater, rod coater and air doctor coater.

In order to improve workability of the film when it is pasted on curved car window glass, the laminated film of the present invention has a heat shrinkage of 1.0 to 5.0% in the machine direction (SMD) and not more than 2.0% in the transverse direction (STD). The SMD is preferably 1.5 to 4.0%, and the STD is preferably not more than 1.5%. When the SMD is less than 1.5% or exceeds 5.0%, the film may be wrinkled when it is stuck to a curved glass surface. When the STD is more than 2.0%, the dimensional stability of the film may deteriorate and the spaces may be formed between the film and the glass surface when the film is stuck to a curved glass surface.

The laminated film of the present invention has a center line average roughness (Ra) of the film surface of 0.005 to 0.05 μm and film haze (H) of not more than 5% for improving transparency. The Ra is preferably 0.01 to 0.04 μm and the H is preferably not more than 4%, more preferably not more than 2%. When the Ra is less than 0.05 μm , the film surface may become susceptible to scratching and nonuniform winding of the film may be caused in the film forming step. When the Ra exceeds 0.05 μm , the roughness degree of the film surface becomes too large and film transparency may be impaired. When the H exceeds 5%, the film may become too high in opaqueness.

The laminated film of the present invention can be produced, for example, by the following process.

First, a polyester (for the intermediate layer) incorporated with a specified amount of a dye and a polyester (for the outermost layers) which may optionally be incorporated with a specified amount of inactive particles are supplied to the respective melt extruders and melted by heating to the temperatures above the melting points of the respective polyesters.

Then, the polyesters are laminated in a state of laminar flow in the die head and extruded from a slit die onto a rotating cooling drum, whereby the extrudate is quenched to a temperature below the glass transition points of the polyesters and solidified to obtain a substantially amorphous non-oriented sheet. In this operation, an electrostatic pinning method and/or a liquid coating adhesion technique are preferably employed for enhancing adhesion between the sheet and the cooling drum to improve planarity of the sheet.

Next, the said sheet is stretched biaxially to obtain a film. In this case, it is preferred that the sheet is first stretched 2 to 6 times in the machine direction at 70 to 145°C, then further stretched 2 to 6 times in the transverse direction at 90 to 160°C and heat-treated at 150 to 250°C for 1 to 600 seconds. The film is also preferably relaxed 0.1 to 20% in the machine and/or transverse directions in the highest temperature zone of the heat-treatment and/or the cleaning zone at the terminal of the heat-treatment. If necessary, re-stretching in the machine and transverse directions may be conducted.

BEST MODE FOR PERFORMING THE INVENTION

The present invention is described in more detail by showing the embodiments thereof, but it is to be understood that the present invention is not limited to these embodiments and receptive to ordinary changes and modifications in the technical field of the present invention without departing from the scope of the present invention. The physical properties of the products were determined by the following methods.

(1) Viscosity (IV)

1 g of polymer was dissolved in 100 ml of a phenol/tetrachloroethane (1/1 by weight) mixed solvent, and the viscosity of this solution was measured at 30°C.

(2) Thickness of each layer of the film

A small piece of each sample film was fixed with an epoxy resin and cut by a microtome, and the film section was observed by the transmission electron micrographs. In the micrographs, the interface is observed as two bright and

dark stripes substantially parallel to the film surface. The distance from the interface of the two stripes to the film surface was measured from 10 micrographs and the average of the measured values was shown as the layer thickness.

(3) Average particle size

The particle size was measured according to the precipitation method based on the Stokes' law using a centrifugal precipitation type particle size distribution meter ("SA-CP3" mfd. by Shimadzu Corp.). The value of 50% of the integration (based on the volume) in the equivalent globularity distribution of the particles obtained by the above measurement was shown as average particle size.

(4) Heat shrinkage (SMD and STD)

Using a circulating hot air oven (mfd. by Tabai Seisakusho Ltd.), each 25 μm thick no-tension sample film was heat-treated in an atmosphere of 180°C for 5 minutes and the film lengths in the machine direction (SMD) and in the transverse direction (STD) before and after the heat-treatment were measured. Heat shrinkage was calculated from the following equation, and the average of the measurements on 5 samples was shown.

$$\text{Heat shrinkage (\%)} = (l_0 - l_1) / l_0 \times 100$$

In the above formula, l_0 indicates sample length (mm) before heat treatment, and l_1 indicates sample length (mm) after heat treatment. In case where l_0 became smaller than l_1 (in the case of expansion), the measured value was expressed with a minus mark (-).

(5) Center line average roughness (Ra)

Center line average roughness (Ra) of the film surface was determined according to JIS-B0601 using a surface roughness tester SE-3F mfd. by Kosaka Kenkyusho KK. Feeler end radius = 2 μm ; load = 3 mg; cut-off = 0.08 mm.

(6) Film haze

Cloudiness of the film was determined according to JIS-K7105 using a turbidity meter NDH-300A mfd. by Nippon Denshoku Kogyo KK.

(7) Color shading

Visible light transmittance of the film was measured in the width direction of the film at intervals of 10 cm at ten points according to JIS-A5759, and color shading was rated according to the following criterion:

○: $T_v(\text{min})/T_v(\text{max}) \leq 2\%$

X: $T_v(\text{min})/T_v(\text{max}) > 2\%$

$T_v(\text{min})$ = minimum value of visible light transmittance in the measurements; $T_v(\text{max})$ = maximum value thereof.

(8) Workability

The condition of the wrinkles and the spaces in the periphery formed after pasting the film on curved car window glass was observed, and workability of the film was rated according to the following criterion:

○: No wrinkle formed, and the spaces in the periphery were uniform.

X: The film was wrinkled, and the spaces in the periphery were non-uniform.

(9) Adherence to hard coat (HC)

The film surface was coated with a hard coating agent of the composition shown below by a #20 bar, then dried at 90°C for one minute to remove the solvent, and further dried by irradiation with light from a high-pressure mercury arc lamp under the following conditions: output = 120 W/cm; irradiation distance = 15 cm; rate of movement = 10 m/min, to form a 9 μm hard coat. Then the hard coat was crosscut to form 100 squares, each being one inch wide, and subjected to a peel test by a 90° pull-up method (rate of pulling: 2 inch/min), and adherence was evaluated according to the fol-

lowing criterion:

○: number of squares which peeled off ≤ 5

5 △: $5 < \text{number of squares which peeled off} < 20$

X: number of squares which peeled off ≥ 20

Hard coat composition

10

Acrylic resin (Seikabeam EXY-26(S) mfd. by Dainichi Seika Kogyo KK): 30 parts by weight

Methyl ethyl ketone: 35 parts by weight

Toluene: 35 parts by weight

15 (Preparation of polyester (A))

100 parts by weight of dimethyl terephthalate, 60 parts by weight of ethylene glycol and 0.09 part by weight of magnesium acetate tetrahydrate as catalyst were supplied to and reacted in a reactor, initiating the reaction at 150°C and raising the reaction temperature gradually with evaporation of methanol to reach 230°C in 3 hours. 4 hours later, the ester exchange reaction was substantially completed. To the resulting reaction mixture were added 0.04 part by weight of ethyl acid phosphate, 0.04 part by weight of antimony trioxide and 0.05 part by weight of silica particles having an average particle size of 1.85 μm to carry out a polycondensation reaction for 4 hours. The reaction temperature was gradually raised from 230°C till reaching 280°C while the reaction pressure was gradually lowered from normal pressure till finally reaching 0.3 mmHg. Upon passage of 4 hours from start of the reaction, the reaction was stopped and the produced polymer was discharged out under nitrogen gas pressure. Viscosity of the obtained polyester was 0.65.

(Preparation of polyester (B) and polyester (B1))

30 The same procedure as used for the preparation of polyester (A) was conducted except that the polycondensation reaction was carried out for 3 hours and 15 minutes without adding silica particles to obtain a polyester (B) with a viscosity of 0.53. This polyester (B) was further subjected to solid phase polymerization under the conditions of 225°C and -0.3 mmHg for 15 hours to obtain a polyester (B1) having a viscosity of 0.78.

(Preparation of polyester (C))

35

Using a vented double-screw extruder, 0.4 part by weight of a red dye ("Diaresin Red HS" produced by Mitsubishi Chemical Corporation), 0.8 part by weight of a blue dye ("Blue H3G" produced by Mitsubishi Chemical Corporation) and 0.3 part by weight of a yellow dye ("Yellow F" produced by Mitsubishi Chemical Corporation) were melt mixed with 100 parts by weight of the dried polyester (B1) to obtain a polyester (C) having a viscosity of 0.61.

40

(Preparation of polyester (D))

45 The same procedure as used for the preparation of polyester (A) was conducted except that instead of the silica particles of 0.05 part by weight having an average size of 1.85 μm , the silica particles of 0.05 part by weight having an average size of 3.24 μm were used to obtain a polyester (D).

(Preparation of polyester (E))

50 The same procedure as used for the preparation of polyester (A) was conducted except that instead of the silica particles of 0.05 part by weight having an average size of 1.85 μm , the silica particles of 0.2 part by weight having an average size of 1.85 μm were used to obtain a polyester (E).

Example 1

55

Polyester (C) dried at 180°C for 4 hours was supplied to a main single-screw extruder set at 285°C while polyester (A) was supplied to a vented double-screw sub-extruder set at 285°C, and they were extruded into the form of a sheet, with polyester (A) being so distributed that it would be present in the two layers (outermost layers) on both sides of the polyester (C) layer, and rapidly cooled and solidified on a rotating cooling drum with a surface temperature of

30°C to obtain a 342 μm thick amorphous sheet. This amorphous sheet was stretched 3.6 times in the machine direction at 83°C and 3.8 times transversely at 90°C, then heat treated at 225°C for 3 seconds and relaxed 5% at 185°C for 2 seconds to obtain a 3 μm /19 μm /3 μm three-layer biaxially oriented film with an overall thickness of 25 μm .

5 Example 2

The same procedure as defined in Example 1 was conducted except that, after 3.6-fold stretching in the machine direction at 83°C, an aqueous coating material comprising 65 parts by weight of a polyurethane resin ("Hydran AP-40" produced by Dainippon Ink and Chemicals Inc.), 20 parts by weight of a polyester resin ("Finetex ES-670" produced by Dainippon Ink and Chemicals Inc.), 10 parts by weight of a melamine crosslinking agent ("Beckamine J-101" produced by Dainippon Ink and Chemicals Inc.) and 5 parts by weight of colloidal silica ("Snowtex YL" produced by Nissan Chemical Industry Co., Ltd.) was applied on one side of the sheet to a coating thickness after drying of 0.1 μm , and then the sheet was further stretched 3.8 times in the transverse direction at 93°C to obtain a biaxially stretched film.

15 Comparative Example 1

The same procedure as defined in Example 1 was conducted except that a mixture of 33 parts by weight of polyester (A) and 67 parts by weight of polyester (C) was supplied to the sub-extruder instead of supplying polyester (A) alone to obtain a biaxially stretched film.

20 Comparative Example 2

The same procedure as defined in Example 1 was conducted except that layer thickness was altered to be 0.1 μm /24.8 μm /0.1 μm to obtain a biaxially stretched film.

25 Comparative Example 3

The procedure of Example 1 was carried out except that layer thickness was altered to be 11 μm /3 μm /11 μm to obtain a biaxially stretched film.

30 Comparative Example 4

The same procedure as defined in Example 1 was conducted except that, after transverse stretching, the sheet was heat-treated at 240°C for 3 seconds and then relaxed 12% at 185°C for 2 seconds to obtain a biaxially stretched film.

35 Comparative Example 5

The procedure of Example 1 was carried out except that, after transverse stretching, the sheet was heat-treated at 210°C for 3 seconds and then relaxed 12% at 185°C for 2 seconds to obtain a biaxially stretched film.

40 Comparative Example 6

The same procedure as defined in Example 1 was conducted except that after heat treatment at 225°C for 3 seconds, no relaxing treatment was conducted to obtain a biaxially stretched film.

45 Comparative Example 7

The same procedure as defined in Example 1 was conducted except that polyester (D), instead of polyester (A), was supplied to the sub-extruder set at 285°C to obtain a biaxially stretched film.

50 Comparative Example 8

The same procedure as defined in Example 1 was conducted except that instead of polyester (A), polyester (E) was supplied to the sub-extruder at 285°C to obtain a biaxially stretched film.

The properties of the obtained biaxially stretched polyester films are shown collectively in Table 1.

Table 1

	Example 1	Example 2	Comp. Example 1	Comp. Example 2	Comp. Example 3
CA/CB	0	0	0.7	0	0
DA/DB	0.24	0.24	0.24	0.01	0.88
SMD	3.5	3.5	3.4	3.2	3.4
STD	-0.7	-0.6	-0.6	-0.6	-0.7
Ra	0.023	0.024	0.022	0.031	0.021
H	1.5	1.6	1.6	0.9	3.5
Tenter contamination	○	○	×	×	○
Color shading	○	○	○	○	×
Workability	○	○	○	○	○
Adherence to HC layer	△	○	△	△	△
Comprehensive evaluation	○	◎	×	×	×

Table 1 (Continued)

	Comp. Example 4	Comp. Example 5	Comp. Example 6	Comp. Example 7	Comp. Example 8
CA/CB	0	0	0	0	0
DA/DB	0.24	0.24	0.24	0.24	0.24
SMD	0.5	7.5	2.3	3.4	3.5
STD	0.7	-0.3	4.0	-0.6	-0.6
Ra	0.022	0.023	0.023	0.056	0.034
H	1.6	1.6	1.5	3.8	6.7
Tenter contamination	○	○	○	○	○
Color shading	○	○	○	○	○
Workability	×	×	×	○	○
Adherence to HC layer	△	△	△	△	△
Comprehensive evaluation	×	×	×	×	×

INDUSTRIAL APPLICABILITY

According to the present invention, there is provided an oriented laminated polyester film for pasting on car window, which polyester film has a dye-incorporated intermediate layer(s), which film is free from the problem of contamination by the dye during manufacture thereof, shows excellent workability when applied on curved glass of an automobile and also has excellent transparency.

Claims

1. An oriented laminated polyester film for pasting on car window, comprising at least three layers including intermediate layer(s) being incorporated with a dye, which laminated polyester film satisfies the following formulae ① to ⑥ simultaneously:

$$CA/CB \leq 0.5 \quad (1)$$

$$0.02 \leq DA/DZ \leq 0.8 \quad (2)$$

$$1.0 \leq SMD \leq 5.0 \quad (3)$$

$$STD \leq 2.0 \quad (4)$$

$$0.005 \leq Ra \leq 0.05 \quad (5)$$

$$H \leq 5 \quad (6)$$

wherein CA represents a dye concentration (%) in the outermost layers on both sides, in case where the dye concentrations in the outermost layers are different, CA represents a dye concentration the outermost layer with a higher dye concentration; CB represents a dye concentration (%) in the intermediate layer, in case where there exist plural intermediate layers, CB represents an average of the dye concentrations in the layers excluding the outermost layers on both sides; DA represents a sum of the thicknesses (μm) of the outermost layers; DZ represents an overall thickness (μm) of the whole layers; SMD represents a heat shrinkage (%) in the machine direction of the film when heat-treated at 180°C for 5 minutes; STD represents a heat shrinkage (%) in the transverse direction of the film when heat-treated at 180°C for 5 minutes; Ra represents a center line average roughness (μm) of the film surface; and H represents film haze (%).

2. An oriented laminated polyester film according to Claim 1, wherein the ratio of DA/DZ in the formula (2) is 0.08 to 0.6.
3. An oriented laminated polyester film according to Claim 1, wherein the ratio of DA/DZ in the formula (2) is 0.15 to 0.5.
4. An oriented laminated polyester film according to any one of Claims 1 to 3, wherein a coating layer and a hard coat layer are provided successively on the surface of one of the outermost layers, and said coating layer has an enhanced adhesion property against the hard coat layer.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP97/04397

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl⁶ B32B27/36, B60J1/00-3/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl⁶ B32B27/36, B60J1/00-3/06, B32B7/00-7/14

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926 - 1996	Jitsuyo Shinan Toroku
Kokai Jitsuyo Shinan Koho	1971 - 1998	Koho
Toroku Jitsuyo Shinan Koho	1994 - 1998	1997 - 1998

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 08-230126, A (Diafoil Hoechst Co., Ltd.), September 10, 1996 (10. 09. 96), Claims (Family: none)	1 - 4
A	JP, 3001731, Z1 (K.K. Shinsei), June 29, 1994 (29. 06. 94), Claims (Family: none)	1 - 4
A	JP, 01-141735, A (Central Glass Co., Ltd.), June 2, 1989 (02. 06. 89), Claims (Family: none)	1 - 4
A	JP, 07-219131, A (Teijin Ltd.), August 18, 1995 (18. 08. 95), Claims (Family: none)	1 - 4

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

January 23, 1998 (23. 01. 98)

Date of mailing of the international search report

February 10, 1998 (10. 02. 98)

Name and mailing address of the ISA/

Japanese Patent Office

Facsimile No.

Authorized officer

Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)